

Long-time behavior of the $\omega \rightarrow \alpha$ transition in shocked Zirconium: Interplay of nucleation and plastic deformation

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We study the thermally activated, slow conversion of the hysteretically retained ω phase into stable α phase in recovered samples of shocked zirconium. The ω -phase decays in time following an algebraic law, unlike the predictions of the nucleation-growth framework for first order transitions, and residual volume fractions of phases and dislocation densities are related by a power law. We propose an explanation for the annealing mechanism through coupled dynamics of dislocations and phase change. We find that the long-time behavior is controlled by the interplay of dislocations, shear fluctuations, and remnant volume fractions of phases, which lead to an algebraic decay in time. For late time, thermally activated quantities such as the dislocation mobility and nucleation rate set the timescale and control the algebraic behavior, respectively. At high enough temperatures this behavior is effectively indistinguishable from standard Avrami kinetics.

There has been much recent interest in understanding the coupling of phase transformation and deformation processes [1–3]. The group IV elements and especially Zr and Ti, with relatively easily accessible transition temperatures and pressures, have been excellent test beds for investigating aspects of deformation and phase transformations under high pressure and shock [4–11]. Starting from ambient conditions, these metals undergo an hcp (α) to hexagonal (ω) structural transformation under pressure, which on release retains substantial volume fractions of the high pressure ω phase [4, 5, 12, 13]. The volume fraction of ω increases with the peak pressure. The metastable microstructure of coexisting α and ω phases in recovered samples, and the significant hysteresis across the equilibrium phase boundary, are a reflection of the non group-subgroup nature of the first-order shear and shuffle (phonon) driven transformation [14]. In addition, we expect aspects of the slow kinetics and history dependence, affected by defects and heterogeneities, to be consequences of the reconstructive nature of this transformation.

We have previously studied the initial evolution of the retained ω phase in recovered samples of shocked Zr at several temperatures under isothermal annealing conditions using x-ray diffraction measurements [15, 16]. Our principal conclusions were that in the temperature range 430–535K, the activation barriers calculated from a modified Kohlrausch-Williams-Watts relation for the evolution of the volume fraction for the reverse $\omega \rightarrow \alpha$ transformation increased with the peak shock pressure [16]. Molecular dynamics simulations interpreted the changes in activation barrier to be controlled by heterogeneous nucleation from defects, such as dislocations, in the microstructure.

The focus of the current work is to develop a phenomenological model for the *long time behavior* that describes the annealing via a coupled dynamics of dislocations and phase change. We derive an algebraic depen-

dence for the late time evolution of the volume fraction of phases at relatively low temperatures, which in the high temperature regime recovers the standard Avrami kinetics. While the kinetics of high temperature recrystallization is generally well understood [17] and found to follow the established Avrami type sigmoidal profile typical of nucleation and growth processes [18], we show here that slow aging of the retained phase in zirconium at low temperatures involves a more subtle interplay with thermally activated dislocations. This is a mechanism reminiscent of shear-driven martensitic transformations. In the case of transformation induced plasticity (TRIP) it leads to a unique combination of high strength and ductility [25, 26] in steels. Localization of externally applied deformation, shear banding, creates potent sites inside the disappearing phase, on which the new phase can nucleate [25, 26, 31–33]. Here we show that even in the absence of external shear, the thermally activated motion of dislocations can determine fluctuations of plastic shear capable of inducing a martensitic transition that eliminates a metastable phase.

We introduce a simplified model of how this can come about, and we test this framework on experimental data obtained by thermal annealing of recovered shocked Zirconium (hcp α -phase: $P63/mmc$, $c/a = 1.593$; simple hexagonal ω -phase: $P6/mmm$, $c/a = 0.623$). Polycrystalline α -Zr shocked loaded to 8 GPa and 10.5 GPa results in a retained volume fraction of $\sim 60\%$ and $\sim 80\%$ respectively of the metastable ω -phase [15]. When the recovered shocked samples are heated, the data show a slow annealing as well as monotonic relationships between the density of dislocations and the volume fraction of the remnant phase [15]. Transitions of this kind are often described by the Johnson-Mehl-Avrami-Kolmogorov approach [18]. However the standard Avrami test on the data shows, at large times, strong deviations from uniform nucleation and growth behavior and its typical sigmoidal behavior.

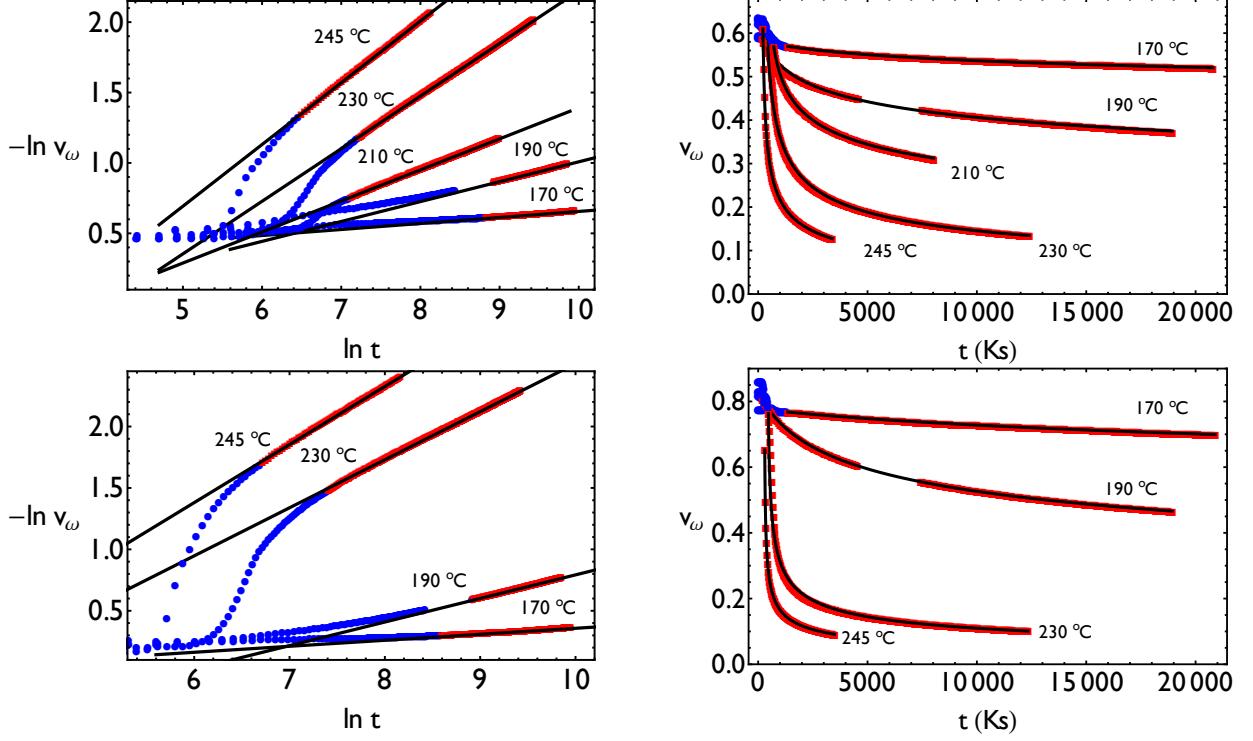


FIG. 1: Fits to volume fraction of the disappearing ω -phase obtained from experimental data taken from the annealing of samples already shocked at 8 GPa (top left) and at 10 GPa (bottom left) using Eq. (1). The left panels of log-log plots show power law behavior at long times. Only data pertaining to long time behavior (red dots) are fitted.

This data, previously reported in the literature [15, 16], is plotted in Fig. 1. We first recognize that at long times the decay is algebraic in time and is well fitted by

$$v_{\omega} = \frac{v_{\omega,0}}{(1 + t/\tau)^{\chi}}. \quad (1)$$

where v_{ω} is the volume fraction of the disappearing ω -phase, and the exponent χ appears to be thermally activated. The key to understanding this algebraic behavior, which is one of our results which we will derive in this work, lies in combining plasticity with nucleation of the new phase. We assume during shock that the material first twins and then nucleates dislocations, which can reach a considerable density before and possibly while the material finally undergoes a transformation toward the ω -phase. These dislocations, may be interpreted as a stabilizing network allowing for retention of the metastable ω -phase. Then, as the sample is heated, the acquired mobility of these thermally activated dislocations can undermine stability, thus providing the driving force for the transformation.

Indeed, martensitic transformations are mediated by a shear strain [25, 26], for example, the retained, metastable austenite phase in TRIP-steel, and its martensitic shear driven transformation [31–33].

Following Stringfellow *et al.* [33], we write the propor-

tionality

$$\dot{v}_{\omega} \propto -v_{\omega}\dot{\gamma}, \quad (2)$$

relating volume fraction to strain rate $\dot{\gamma}$ in the shear-induced nucleation on potent sites created by plastic strain [32]. Stringfellow *et al.* observed that for TRIP steels the strain-induced nucleation occurs at shear band intersections, and included a proportionality constant to account for the nucleation rate of shear bands at low strains. Here the proportionality constant will be related to the temperature dependent dislocation removal rate. In the case, e.g., of TRIP steel, the shear is global and externally applied. In our system, however, the total strain rate is endogenous, and ambient. In particular $\dot{\gamma}$ is not a total derivative, but rather the average of the absolute value of the local strain rates, and thus, in general $\gamma \neq \int \dot{\gamma} dt$.

The experimental data provides average and coarse information on dislocation densities, which can be obtained from averaging the peak widths of the X-ray data [15]. We can relate such information to the local shear rates. Indeed, Kocks and Mecking [34, 35] have introduced a phenomenological equation to relate variations in the shear rate to the density of dislocations:

$$d\rho/d\gamma = c_1\sqrt{\rho} - c_2\rho. \quad (3)$$

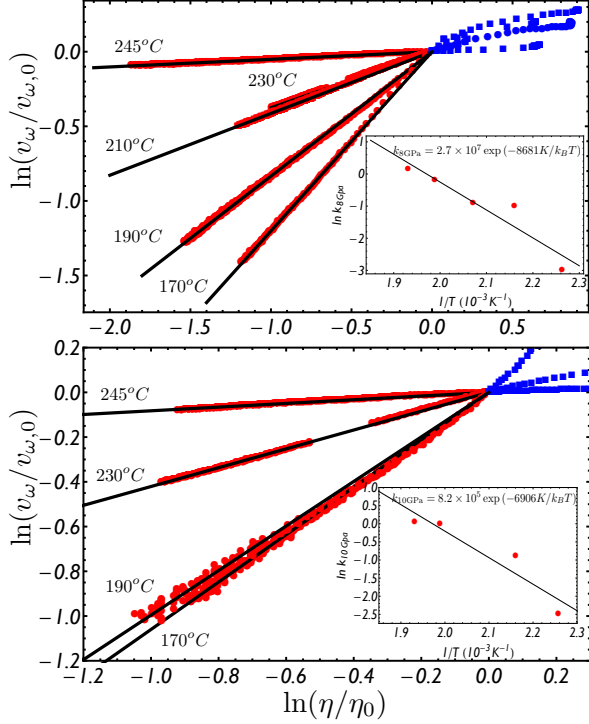


FIG. 2: Eq. (6) reveals the power law behavior for the volume fraction and dislocation density parameter $\eta = \rho - \rho_\infty$ for zirconium shocked at 8 GPa (Top, at temperatures of 170, 190, 210, 230, and 245 C) and 10 GPa (bottom, at temperatures of 170, 190, 230, and 245 C); data in blue are not fitted, as in Fig. 1. Insets: The fitting exponent k , which is the nucleation rate for Eq. (5) obtained from fits to Fig. 2, is a thermally activated nucleation rate; an Arrhenius fit returns higher activation energies for α -phase nucleation in the samples shocked at the lower pressure.

Equation (3) describes the storage (first term) and annihilation (second term) of dislocations in a material subjected to environmental shear, in our case coming from the collective motion of dislocations (plastic shear) and from phase transformation (transformation shear).

In general, the constant c_2 is proportional to the critical annihilation distance for dislocations; the term c_1 , is the subject of much recent research and its dependence on the specificity of the problem is still debated [24]. We can neglect these issues by noting that c_1 simply defines the stationary density of dislocations $\rho_\infty = (c_1/c_2)^2$ at which, in (3), $d\rho/d\gamma = 0$ because of our focus on the asymptotic behavior. We can then eliminate c_1 by introducing $\eta = \rho - \rho_\infty$ and expanding the Kocks-Mecking equation around $\eta \sim 0^+$, thus obtaining in the asymptotic regime $d\eta/d\gamma = -c_2\eta/2$, or equivalently

$$\dot{\gamma} = -\frac{2}{c_2} \frac{\dot{\eta}}{\eta}. \quad (4)$$

Thus from Eq. (2) and Eq. (4) it is immediate to obtain

$$\frac{dv_\omega}{v_\omega} = k \frac{d\eta}{\eta}, \quad (5)$$

which establishes a proportionality between the relative rates of variation of the dislocation density and volume fraction during phase change (here k is a nucleation rate).

Fortunately this interesting result can be tested using experimental data. Indeed, from Eq. (5) we can now obtain a power law relating volume fraction and dislocation density

$$\frac{v_\omega}{v_{\omega,0}} = \left(\frac{\eta}{\eta_0} \right)^k, \quad (6)$$

where the exponent is the nucleation rate k , $\eta_0 = \rho_0 - \rho_\infty$ is the density of mobile dislocations at the beginning of the process, and $v_{\omega,0}$ is the initial volume fraction.

In Fig. 2 we demonstrate the power law behavior of Eq. (6) via a logarithmic plot which is used to fit the constant k : ρ_0 is experimentally given, while ρ_∞ has to be fitted, as the annealing is never complete in these experiments. In the left panels we demonstrate the power law of Eq. (6) via a log-log plot which is used to fit the constant k at large times. Since k is a nucleation constant, we expect it to be thermally activated, or

$$k \propto \exp(-\Delta W/k_B T), \quad (7)$$

with activation energy ΔW .

Indeed Fig. 2 shows the Arrhenius fit for k which returns the values for the activation temperature $T_{8\text{GPa}} = 8.7 \times 10^3 \text{ K} \simeq 0.75 \text{ eV}$ and $T_{10\text{GPa}} = 6.9 \times 10^3 \text{ K} \simeq 0.6 \text{ eV}$, consistent with the results of atomistic calculations [16]. The fact that activation energies for nucleation rates are different in the two cases points to an inherent difference in the microscopic structure of samples shocked at different pressures, in accordance with our previous findings [16].

To deduce the time evolution of the normalized volume fraction $v_\omega(t)$ it is sufficient to know the time dependence of the dislocation density $\rho(t)$. This can be resolved in a coupled dynamics that involves plasticity and phase change. There are two sources of shear: transformation shear γ_t and plastic shear γ_p . The source of plastic shear rate $\dot{\gamma}_p$ is the motion of the dislocations in the ω -phase, and is well known from the Orowan equation [21]

$$\dot{\gamma}_p = b\rho_m w_d, \quad (8)$$

in which w_d is the thermally activated mobility of the mobile dislocations ρ_m , b is the magnitude of the Burgers vector. In our phenomenological approach $\dot{\gamma}$ is not a total derivative, as explained above when introducing the Kocks-Mecking equation, but rather the coarse grained shear, over a sufficiently large region of the *absolute value* of the intensity of the local shear rates. Furthermore the

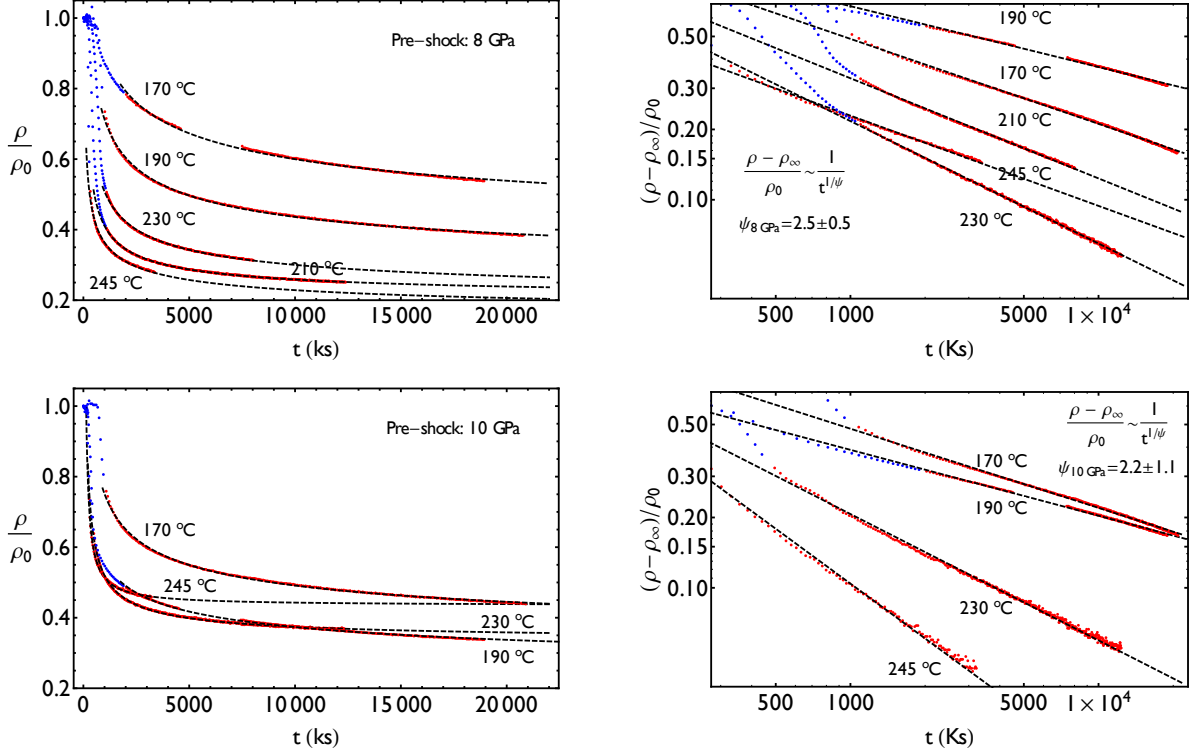


FIG. 3: Fits to Eq. (10) for experimental data of dislocation densities normalized at the initial value as a function of time for samples annealed at different temperatures and schocked at 8 GPa (top panels) and 10 GPa (bottom panels). Log-log plots (right panels) show the algebraic decay from Eq. (10). The fitted remnant density of dislocations ρ_∞ appears scattered amongst samples and temperatures, and is possibly sample dependent [15]; it is however not a relevant parameter in our theory. Data in red are fitted, data in blue are not fitted.

relationship between mobile dislocations ρ_m and the excess dislocations η is unknown to us. In general the mobile dislocations will be less than η as some of the annihilating dislocations might be non-mobile. In the absence of more precise information, we proceed with the reasonable ansatz that the *relative* decrements of mobile dislocations and of dislocations tout-court are proportional, or $d\rho_m/\rho_m = \psi d\eta/\eta$. This, together with the Orowan equation (8) leads us to write

$$\dot{\gamma}_p = c_3 \eta^\psi, \quad (9)$$

with $\psi > 1$ and c_3 proportional to the dislocation mobility w_d .

The other source of shear, the transformation shear γ_t , is associated to the structural change in unit cells of the α and ω phases. Clearly, its rate is proportional to the rate of phase change, or $\dot{\gamma}_t = c_4 \dot{v}_\omega$, where v_ω is the volume fraction of the ω phase, and c_4 depends on the geometric parameters of the unit cells in the two phases. Indeed from Eq. (2), we have that in the asymptotic limit most of the shear rate is purely plastic, or $\dot{\gamma}_t/\dot{\gamma} \propto v_\omega \rightarrow 0$. This allows us to approximate $\gamma_p \simeq \gamma$ in Eq. (9). Then, in the approximation of long times, $\rho(t)$ can be found

from (9) and (4) to be

$$\eta = \frac{\eta_0}{(1 + t/\tau)^{1/\psi}}. \quad (10)$$

In Fig. 3, we demonstrate that Eq. (10) fits the data very well. Equation (10) describes a slow, algebraic decline at long times, controlled by the parameter $\tau^{-1} \propto c_3 \propto w_d$, which depends on temperature through the thermally activated mobility of dislocations w_d . Interestingly, the decay is faster at higher temperatures (because τ of Eq. (10) depends on the activated dislocation mobility) and for samples pre-shocked at higher pressure (because more dislocations have been nucleated to begin with). Yet the value of the exponent ψ from Eq. (9), which represents the ratio of relative decrement between mobile dislocations and dislocations proper is *almost* the same in all cases and close to the value of $\psi = 2.5$.

Equation (1) can now finally be deduced from (6) and (10) which imply $\chi = k/\psi$: the exponent χ , which controls the long time algebraic decay of the remnant volume fraction, is thus also, like k , an activated quantity that follows an Arrhenius law. This result suggests the following: *while the dislocation mobility w_d sets the timescale, the nucleation rate k controls the algebraic decay of the*

residual volume fraction of the ω -phase. As both quantities are thermally activated, higher temperature implies not only a smaller timescale (controlled by w_d) but also a larger relative decrement for the same relative increment of time (controlled by k).

Our work elucidates the limits of the standard nucleation and growth framework [18] which can be relevant to other systems. We have seen that the algebraic approach to equilibrium is a consequence of the coupled dynamics of phase transformation and dislocations. When the temperature is high enough, the conventional Avrami formalism can still provide a reasonable description. Let us see how that can come about.

From Eq. (1) we can write directly

$$\frac{\dot{v}_\omega}{v_\omega} = -\frac{k}{\psi\tau} \left(\frac{v_\omega}{v_{\omega,0}} \right)^{\frac{\psi}{k}}, \quad (11)$$

which shows that the total nucleation rate is not constant, as in usual nucleation and growth, but rather a power law of the concentration of the disappearing phase. However, at high temperatures, k becomes exponentially large and $(v_\omega/v_{\omega,0})^{\psi/k} \simeq 1$ unless $v_\omega/v_{\omega,0}$ is very small, say below the experimental error. Then the nucleation rate can be well approximated by the constant value $k/\psi\tau$. Of course, mathematically, the behavior at long times will always become algebraic. However, for all practical purposes at large enough temperatures, that might happen only when the residual volume fraction is as low as to be negligible or unmeasurable, while in general Eq. (11) shows that the measured nucleation rate might in fact appear constant at any experimentally reasonable value of the volume fraction.

In the context of the behavior of v_ω vs η , described by Eq. (6), at high temperature and thus large k corresponds a sudden drop in volume fraction on a timescale $\tau\psi/k$, while the density of dislocations would show little change, its timescale being τ ; thus a standard nucleation approach can be effectively regained when the two dynamics, for phase transformation and dislocations, become decoupled.

In conclusion, we show that a coupled dynamics of plasticity and nucleation leads to an algebraic transformation law in which dislocation mobility defines the timescale whereas the nucleation rate on potent sites controls the power law behavior. Beside proposing a possible explanation for the slow aging of the metastable ω -phase in Zirconium, we are also elucidating one of the mechanisms by which, more generally, the accepted nucleation and growth framework can mask a more complex dynamics, one that becomes apparent only at lower temperatures. This is most likely not an isolated case and similar mechanisms may be at work in the aging of metastable multiphase materials under extreme thermodynamic and boundary conditions, such as at nanoscale or in film geometries.

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